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VI.

RESEARCHES ON THE VOLATILE HYDROCARBONS.

By C. M. Warren.

Communicated May 12, 1868.*

III.—ON THE VOLATILE HYDROCARBONS IN PENNSYLVANIA PETROLEUM.—Part I.

The results recorded in this paper were obtained previously to the publication of a memoir "On the Influence of CH_2 on the Boiling-points in Homologous Series of Hydrocarbons," etc., which I had the honor to present to the Academy in 1864.† In that memoir I had occasion, for a special purpose, to introduce, among others, the formulæ of the hydrocarbons that I had separated from Pennsylvania petroleum, but omitting for the time being the data from which these formulæ were deduced, with the intention to follow shortly after with another paper in which these data would be given. Publication was at first delayed for an opportunity to repeat some of the analyses by means of my process for combustion in oxygen gas,‡ (which is specially suited to the analysis of volatile substances,) with the view to obtain more exact results which might throw some light on the question raised in that paper,* as to whether the 1st and 2d series there presented should be considered isomeric. For the same reason, it seemed desirable also, before publication, that the relations of these series should be further studied by at least a preliminary examination of some of the more important chemical properties of the different bodies which they comprise. With no immediate prospect of being able to pursue these inquiries,—already so long deferred from unavoidable causes,—it seems now advisable to publish the results obtained, without relinquishing, however, the hope of continuing the investigation.

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* The manuscript of this memoir was found among the author's papers after his death. The article had been presented to the Academy by title at a meeting held on May 12, 1868, and appears to have been written out in its present shape at that time, with the possible exceptions that one or two brief footnotes may have been added subsequently, and that the style of naming some of the compounds may have been changed. The author's motive for holding back the communication — as indicated by brief marginal notes written in pencil upon his manuscript — seems to have been based on a wish to make one or two new analyses, and to repeat by a process of his invention a few determinations of vapor density, in order that absolute justice might be done to Pelouze and Cahours in his criticism of their work. Broadly considered, the delay appears to have been a case of procrastination pure and simple, for there is evidence that the author had never given up his intention of publishing the paper as it now stands.

† Memoirs of the American Academy, (N. S.) IX. 156.

‡ Proceedings of the American Academy, 1864, p. 251.

Notwithstanding the fact, as above intimated, that some of the results to be presented are not entirely satisfactory, they are published in the belief that they are more nearly correct than the corresponding results that others have obtained in the investigation of this petroleum; and will, therefore, contribute materially to our knowledge of the bodies obtained therefrom. This belief is justified by the circumstance that the different constituents of the petroleum were separated by a process far more searching and reliable than any distillatory process that had been applied to such a mixture; † hence, that the several bodies examined were obtained in a state approximating much nearer to purity than seems possible by any other method of fractional distillation yet devised. As a natural consequence, some of the more important results that I have obtained in the study of this petroleum differ essentially from those of other investigators of the same material, notably those of Pelouze and Cahours, whose researches are often quoted as authority on this subject.‡

Before proceeding to give the experimental results which it is the special object of this paper to furnish, it may be of service, and may excite additional interest in the subject, to recall briefly some of the facts furnished in my former paper, and to specify some of the more striking differences between my results and those of the chemists above mentioned.

In the memoir first above referred to (pp. 166, 167), the hydrocarbons that I have separated from this petroleum are classified in three natural series, designated, provisionally, as 1st, 2d, and 3d series. The first two of these may be conveniently considered as parallel series, since they exist as it were side by side, and in fact extend through and naturally belong to the same portion of the petroleum, and present, moreover, a nearly uniform difference of boiling-point, viz. about 8° C. between any two corresponding or opposite members of the two series, as will appear on inspection of the tables. Both series, however, have in common the boiling-point difference of about 30° between any two contiguous members, corresponding to the common elementary difference of $\text{Є}H_2$, as also shown in the tables referred to. The members of the 3d series have boiling-points ranging from 0° to 150°, and those of the 2d series from about 8° to 128°.

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* See foot-note, page 167.

† "Process of Fractional Condensation," etc., Memoirs of the American Academy, (N. S.) IX. 121.

‡ Comptes Rendus, LIV. 1241, LVI. 505, LVII. 62.

In striking contrast with these results, Pelouze and Cahours found in this portion of the petroleum but one series, or only about one half the number of bodies that I obtained. We do not differ, however, as to the general formula ($\text{Є}_n H_{2n+2}$) of the bodies belonging to this portion of the petroleum. But in regard to the boiling-point difference for the successive terms of the series, which, as already stated, I have shown to be uniformly about 30° in the $\text{Є}_n H_{2n+2}$ Series, we find in their results hardly an approximation to uniformity in this respect. On the contrary, their boiling-point differences, corresponding to an elementary difference of $\text{Є}H_2$, are observed to vary so widely as from 16° or 20° to 38°.

Yet more remarkable is the circumstance that, above 150° (the highest point reached by either of my first two series), in that part of the petroleum embracing my 3d series, in which I find only bodies of the general formula $\text{Є}_n H_{2n}$, they find, on the contrary, none of these, but continue to obtain bodies which they represent as having the same general formula as those belonging to the more volatile portion of the petroleum.* They maintain that the whole liquid portion of the petroleum is made up of one continuous series, having the general formula C_nH_{2n+2}; and, moreover, that the solid paraffines from this source belong also to this series, of which at least there is much reason to doubt.

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* The temperatures here given relate, of course, either to isolated substances, or to sections of the petroleum considered as if composed exclusively of those bodies whose true boiling points have been found to come within the limits of temperature above indicated; not ignoring the fact, however, that during the process of separation, when applied to a mixture that includes all of the three series, some of the 1st and 2d series come off in reality at temperatures considerably above that indicated as the highest limit of these two series, viz. 150°; nor unmindful of the fact, on the other hand, that some of those of higher boiling-point — members of the 3d series — are carried over with the

Concerning a natural product of great importance in itself and in its relations, results so discordant as above indicated should have a careful and impartial examination with reference to the different conditions under which they were respectively obtained, with the view to determine which should be regarded as the more accurate. Having this purpose in view, and with the conviction that the work done does not so much need repetition as to be understood, and believing that the facts that I have to present are sufficient to establish at least the probability of the correctness of the conclusions I have reached, it will be necessary, in the following consideration of the subject, to make such further comparison of their results with my own as the pursuit of the object defined seems to require.

Examination of the Petroleum.

Of the Material employed.—Commercial Products from the Petroleum.

In the investigation of this petroleum I have not operated directly on the crude oil, but upon certain distillates obtained from this on a manufacturing scale. Special care was taken to procure these from a reliable source, and to obtain such as had not been subjected to any chemical treatment; and also such, taken collectively, as would fairly represent the natural product so far as to include in sufficient quantity all of its constituents. A brief description of these crude distillates, indicating their comparative value as sources of supply of the different constituents, may not be void of interest, and may be of service to such, especially, as may have occasion to repeat any portion of the work. This remark is suggested by a statement of Schorlemmer[*] with respect to one of the members of my 1st series, viz. that boiling at 61°.3, that it was not present in the petroleum that he worked upon. After the

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vapors of the more volatile ones, at temperatures below their true boiling-points, or within the range of the 1st and 2d series, their true or natural position in the series not admitting of determination until, by the process of separation, the bodies shall have attained a comparatively high degree of purity.

[*] Philosophical Transactions, 1872, Vol. CLXII. p. 116.

publication of my first memoir, above referred to, this chemist appears to have made a special search for these bodies, which were entirely overlooked in his earlier research, and such of them as he found he seems to have obtained in small proportion,— quite the reverse of my experience. E. g., of the body boiling at 61°.3, which, as stated, he did not find, the proportion of my product, as compared with that boiling at about 68°, was as 7 to 8.

In the earlier stage of the distillation, in the manufacture of "illuminating oil" or "refined petroleum," (a medium product, amounting to some 70 per cent of the crude material,) there is obtained, as is well known, a considerable quantity — frequently about 15 per cent — of a colorless and highly volatile liquid, variously known in commerce as naphtha, spirits of petroleum, and, improperly, as benzine. Although containing some of the substances that more especially characterize the heavier or medium portion of the petroleum, the larger proportion of this naphtha is composed of bodies whose boiling-points range from 0° to 150°, these being the limits of my provisional 1st and 2d series, and is therefore a convenient source from which these for the most part may be obtained. Some manufacturers separate this naphtha, either by a second distillation or during the distillation of the crude petroleum, into two parts, a "light" and a "heavy naphtha." The former of these is the product commercially known in the United States as "Gasolene," which is more or less extensively employed, mixed as vapor with atmospheric air, as a substitute for coal gas. It was from this "gasolene" or "light naphtha," having the specific gravity 0.65 at 15° C, that the hydrocarbons comprised in my 1st and 2d series were chiefly procured. Although this product contains a larger proportion of some of the lower or medium members of these two series,— as its low specific gravity and high degree of volatility would indicate,— it also contains considerable quantities of the higher ones; but the latter may be obtained in greater abundance from the "heavy naphtha," and in notable quantity also from the medium product described as "illuminating oil," from which to a considerable extent it may be conveniently procured while operating to obtain the members of the 3d series, of which this product is chiefly composed.

In the manufacture of these naphthas, a large portion of the two most volatile constituents of the petroleum — those boiling at 0° and 8° respectively — is generally allowed to escape condensation, and to a considerable extent, also, the two next higher ones, boiling at 30° and 38°. Since the first two here mentioned, when isolated from those of higher boiling-points, are gases at the common temperature, a mixture of these may be more readily obtained in large quantity from a manufactory, by conducting the vapors from the still into a condenser maintained at a low temperature, — being the product introduced by Dr. Henry J. Bigelow for a local anæsthetic under the name of Rhigolene.* The large preponderance, in this product, of these most volatile constituents of the petroleum might be inferred from the fact, as stated by him, that when continuously dropped on the bulb of a mercurial thermometer evaporation is so rapid as to cause the mercury to fall to —7° within 5 to 10 seconds.

Of the Results of Fractional Condensation.

For convenience of reference I will here repeat, with slight modifications, some of the tables from my previous memoir. These exhibit the three homologous series of hydrocarbons that I have separated from the petroleum, together with their boiling-points, the differences of boiling-point corresponding to an elementary difference of $\text{Ȼ}H_2$, and their formulæ, — the data for which are given on the following pages.

Hydrocarbons from Pennsylvania Petroleum.

1. Marsh-gas Series.

Name of Substance.	Formula. Ȼ_nH_{2n+2}	Boiling-point.	Elementary Difference.	Difference of Boiling-point found.	Range of Temperature within which Substance all distilled.
		°		°	°
Butyl Hydride	Ȼ_4H_{10}	0.0 †	—	—	—
Amyl "	Ȼ_5H_{12}	30.2	$\text{Ȼ}H_2$	30.2	1.5
Hexyl "	Ȼ_6H_{14}	61.3	$\text{Ȼ}H_2$	31.1	0.8
Heptyl "	Ȼ_7H_{16}	90.4	$\text{Ȼ}H_2$	29.1	1.0
Octyl "	Ȼ_8H_{18}	119.5	$\text{Ȼ}H_2$	29.1	1.0
Nonyl "	Ȼ_9H_{20}	150.8	$\text{Ȼ}H_2$	31.3	0.8

150.8 ÷ 5 = 30°.16

Average increment of boiling-point for the addition of CH_2 = 30°.16.

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* Chemical News, 1866, XIII. 244.

† Ronald's determination.

2. Isomeric (?) with the Marsh-gas Series.

Name of Substance.	Formula. $€_nH_{2n+2}$	Boiling-point.	Elementary Difference.	Difference of Boiling-point found.	Range of Temperature within which Substance all distilled.
Iso-Butyl Hydride	$€_4H_{10}$	° 8–9	—	° —	° —
" Amyl "	$€_5H_{12}$	37.0	$€H_2$	29.0	0.4
" Hexyl "	$€_6H_{14}$	68.5	$€H_2$	31.5	0.6
" Heptyl "	$€_7H_{16}$	98.1	$€H_2$	29.6	1.2
" Octyl "	$€_8H_{18}$	127.6	$€H_2$	29.5	1.5

119.6 ÷ 4 = 29°.9

Average increment of boiling-point for the addition of CH_2 = 29°.9.

3. Ethylene Series.

Name of Substance.	Formula. $€_nH_{2n}$	Boiling-point.	Elementary Difference.	Difference of Boiling-point found.	Range of Temperature within which Substance all distilled.
Rutylene	$€_{10}H_{20}$	° 174.9	—	° —	° 1.7
Margarylene	$€_{11}H_{22}$	195.8	$€H_2$	20.9	1.5
Laurylene	$€_{12}H_{24}$	216.2	$€H_2$	20.3	2.2

41.2 ÷ 2 = 20°.6

Average increment of boiling-point for the addition of CH_2 = 20°.6.

Having already given in one of the memoirs above referred to a detailed description of the process devised for the separation of the constituents of such complex mixtures of liquids as that under consideration, and which was employed in this research, these details are here omitted. I should state, however, that in conducting the separations in this case, the same exhaustive method was pursued as therein described.* By this treatment, the intermediate small fractions lying between the prominent ones were repeatedly and so thoroughly worked over as to prove the absence of other bodies than those described, i. e. in quantities appreciable by fractional condensation. I do not, however, ignore the fact that small quantities of other bodies might be present and escape detection. That any appreciable constituent of that part of the petroleum worked upon was overlooked in this investigation is the more improbable from the fact that, in consequence of the discovery of the new series isomeric with the hydrides, vastly more time and labor were given to these separations than are ordinarily required, or than would have been necessary otherwise. The extremely small difference of boiling-point between the corresponding or opposite members of these two parallel series has necessitated a most thorough and critical examination, requiring a vast number of redistillations, each extending over the whole range of fractions,— a fraction being taken for every degree of temperature,— and this extremely tedious process was continued until the small intermediate fractions, as before stated, had become too small to admit of being further operated upon; and until the boiling temperature of the large fractions herein treated of had ceased to undergo further change by this treatment. This course was deemed indispensable, — regardless of the large expenditure of time involved,— since nothing less could suffice to remove all doubt as to the existence of the newly discovered series, and insure for the different substances that degree of purity requisite for any satisfactory study of their individual properties.

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* Memoirs of the American Academy, (N. S.) IX. 130–134.

I have laid special stress on the circumstance here related, since it appears, on comparison of my results with those of Pelouze and Cahours, that they claim to have found one more body between about 120° and 236° than I have been able to discover. Either I have overlooked in my analysis one constituent of the petroleum between these limits of temperature, or they have described one having no existence therein; in this connection, for obvious reasons, my newly discovered series of isohydrides is of course not taken into account. To facilitate a comparison of their results with my own, as the latter are exhibited in the preceding tables, I will here introduce the following table prepared by me for this purpose.*

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* At this date the nomenclature here employed may appear antiquated; but since this does not affect the intrinsic value of the paper, I have preferred to let it pass through the press as written several years ago.

Tabular Statement of the Formulæ and Boiling-points of the Constituents of Pennsylvania Petroleum, as determined by Pelouze and Cahours.

Name of Substance.	Formula ($Ꞓ_nH_{2n+2}$)	Boiling-point.	Elementary Difference.	Difference of Boiling-point found. (Average.)
Hydride of Butyl	$Ꞓ_4H_{10}$	° 5–10	—	° —
" Amyl	$Ꞓ_5H_{12}$	30	$ꞒH_2$	22.5
" Caproyl	$Ꞓ_6H_{14}$	68	$ꞒH_2$	38.0
" Œnanthyl	$Ꞓ_7H_{16}$	92–94	$ꞒH_2$	25.0
" Capryl	$Ꞓ_8H_{18}$	116–118	$ꞒH_2$	24.0
" Pelargonyl	$Ꞓ_9H_{20}$	136–138	$ꞒH_2$	20.0
" Rutyl	$Ꞓ_{10}H_{22}$	160–162	$ꞒH_2$	24.0
" ——	$Ꞓ_{11}H_{24}$	180–184	$ꞒH_2$	21.0
" Lauryl	$Ꞓ_{12}H_{26}$	196–200	$ꞒH_2$	16.0
" Cocinyl	$Ꞓ_{13}H_{28}$	216–218	$ꞒH_2$	19.0
" Myristyl	$Ꞓ_{14}H_{30}$	236–240	$ꞒH_2$	21.0
" ——	$Ꞓ_{15}H_{32}$	255–260	$ꞒH_2$	19.5

As their results, indicated by the above table, differ so widely from mine, not only in regard to boiling-points in several instances, but also in the important matters of vapor density and elementary constitution corresponding thereto, as will be shown further on, it is impossible for me to determine with any degree of certainty which of the several bodies they describe should be chosen as the one whose existence in the petroleum must be questioned; for my results, I trust, will show conclusively that one of their number must be discarded, and that consequently the formula of the rejected member would naturally fall to the one next above, and the formula of this in turn to the next higher, and so on, changing the formulæ of all the higher members of their series. Since, however, they have not described a greater number of bodies within the range of temperature embraced by my 3d series — the $Ꞓ_nH_{2n}$ series — than were found by me, although we differ widely as to their constitution; and since their boiling-points in this part of the petroleum are less at variance with mine, I am induced to consider that the spurious body in question is more probably one of the two lying between 120° (a point at which we agree very nearly both as to boiling-point and vapor density) and 175°, the point at which my 3d, or $€_nH_{2n}$ series, begins. It matters little which of these it is, and we will therefore assume it to be the lower one of the two, or their first above 120°, viz. that boiling at 136°–138°, which they represent by the formula $€_9H_{20}$. This formula, it may be observed, is the same that I have given to a body boiling at about 150°, finding none intermediate between this and 127°; the latter, however, is not of the same series, being isomeric with the body boiling at 120°, having the formula $€_8H_{18}$.

The question as to the existence in the petroleum of a body whose boiling-point lies between the limits of temperature indicated, viz. 127° and 150°, is seen to be of more importance when it is considered, as above stated, that it involves the question as to the constitution or correctness of the formula or formulæ of the higher member or members of the series; and especially so if it be held that the $€_nH_{2n+2}$ series in petroleum, instead of terminating at 150°, as I maintain, is really so extensive as alleged by Pelouze and Cahours,— they having already assigned to it seven bodies of boiling-points above 118°, the highest of which boils at 260°; and assumed, as already stated, that this series goes on uninterrupted to, and includes, the solid paraffines. For if, as I maintain, the petroleum does not contain the body in question, and if the $€_nH_{2n+2}$ series *has* the wide range which they assert, then it must follow that the formulæ assigned by them to these seven or more bodies would each require the deduction of $€H_2$, and hence that their determinations would become almost worthless, since so great a discrepancy would indicate for the substances a degree of impurity sufficient to destroy confidence in the results that they obtained in the further study of these bodies. I have assumed, in this consideration, that the lower members of the series have been correctly determined, there being no disagreement between their determination and my own of the formula — $€_8H_{18}$ — of the body boiling at 119°.5 (116°–118° by their determination), nor of the formulæ of the lower members of the series.

Trusting that a comparative examination of the results presented in this paper, giving due consideration to the fact of the greater efficiency of the process employed in my proximate analysis of the petroleum, will leave no room for doubt on the questions presented, and will confirm the views above stated, I will now proceed to give details of the elementary analyses, and of the experiments to determine such of the physical properties of the individual bodies as are usually relied upon to identify or characterize bodies of this class. I would here state, however, once for all, that, unless specially mentioned, no one of the bodies operated upon had received any chemical treatment except that of boiling with sodium.

Of the Analyses and Physical Properties of the different Bodies separated from the Petroleum.

1. BUTYL HYDRIDE AND BUTYL ISO-HYDRIDE = C_4H_{10}.*

My examination of butyl hydride and its isomeric associate in the petroleum has been more limited than that of the other members of the series to which they respectively belong. As these bodies could at any time be readily obtained in larger quantity at a manufactory, in the manner above described, I omitted to make further use of the small quantities that I had incidentally collected than to determine their boiling-points, and of one of them, viz. iso-hydride of butyl, the specific gravity, which was found to be 0.6107 at 0°. Ronalds has found the specific gravity of the other, viz. hydride of butyl, to be 0.600 at 0°.

In the original publication of the above tables, the boiling-point of butyl hydride was given, with an interrogation point, as 0°; for although I had observed that a mixture of the two bodies began to boil at about this temperature, it was on theoretical considerations that this precise figure was given, and, of course, a more positive statement would not be justifiable. That this, however, is at least very nearly its true boiling-point, has since been confirmed by Ronalds,† who has made a special study of the most volatile part of the petroleum, and who states that it begins to boil at 0°. It does not appear, however, that he made a better separation of the two bodies, for he failed even to detect the presence of butyl iso-hydride, and could not therefore have made an attempt to separate it. Moreover, he worked by the old method. Ronalds, however, collected a liquid boiling between 6° and 8°, specific gravity 0.6004, but did not regard it as a distinct body, but merely as a mixture of butyl hydride and amyl hydride, Є_5H_{12}, which latter boils at about 30°.

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* Studied in 1868 by E. Lefebvre, Jahresb., 1868, p. 329.

† Journal of the Chemical Society, London, 1865.

It is needless to remark that to call this a mixture, in the broad sense that Ronalds has done, does not accord with my experience. The boiling-point, 8°–9°, that I found for butyl iso-hydride was the result of an actual determination in the usual manner. The material employed for this purpose had been repeatedly and carefully distilled through my regulated condenser; but it had finally become so reduced in quantity as to necessitate suspension of the process of fractionation before the separation was so nearly complete as is claimed for the bodies of higher boiling-point. Nevertheless, it is believed to have been sufficiently pure to justify the conclusion — supported also by analogy — that there is a constituent of the petroleum boiling at about 8° to 9°, as I had stated. I would not, however, be understood to maintain that this body, as obtained, contained no admixture of butyl hydride, or even of amyl hydride, for doubtless it contained both of them to some extent. I only contend that probably neither was present in sufficient quantity to materially, if indeed perceptibly, influence the boiling-point, and consequently that the elevation of the boiling temperature above 0°, or that of butyl hydride, was not due to the presence of amyl hydride, as we should infer from Ronald's statement, but rather to the fact that it was mainly composed of butyl iso-hydride, which he overlooked.

I may remark in this connection that a similar view is held in regard to the purity of the other bodies that I have separated from the petroleum; although the purification of most or many of these was carried to the extreme practicable limit, they doubtless still remained mixtures, but probably in such relative proportions as to admit of correct, or at least very nearly correct, determinations of their boiling-points. That such was the probable condition of these bodies is not merely a theoretical opinion based on my own observations. The experiments of Berthelot[*] show that mixtures of neutral liquids whose boiling-points differ by 20°–30°, being mixed in such proportion that the least volatile amounts to 8 or 10 per cent, do not admit of separation by distillation under ordinary pressure, and will frequently, if not always, be found to comport themselves like homogeneous substances.

Berthelot's results have since been confirmed by Alluard,[†] who found that ether mixed with one tenth of its weight of bi-sulphide of carbon, not only had a constant boiling-point, but that this was *the same as that of pure ether*. He also made similar observations on mixtures of bi-sulphide of carbon and alcohol, and alcohol and water.*

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[*] Comptes Rendus, LVII. 430.

[†] Comptes Rendus, LVIII. 84.

In the case of a mixture of two liquid bodies whose physical properties differ so little as those of the hydrides and iso-hydrides under consideration, probably a larger proportion of the lesser constituent of the mixture may be present without affecting the boiling-point of the larger one, than was shown in the experiments of Berthelot and Alluard; and, in such a case, it may be found impossible to purify a body sufficiently for some of the requirements of an investigation. But the fact that the constituents of such a mixture may be brought into such proportions by fractional condensation as to give the true boiling-point of the larger constituent, must nevertheless be regarded as of great importance in many cases, since the boiling-point is frequently an invaluable means of controlling the formulæ in homologous series; and especially so when the body under examination contains so large an admixture of foreign substance that the vapor density and ultimate analysis cannot be relied upon, which might often occur. Evidently these are considerations to be taken into account in passing judgment upon the value of results of an investigation of a mixture of liquids based on a proximate analysis by any method of fractional distillation; and it cannot be too strongly maintained, that constancy of boiling-point, even if considered only as an approximative indication of the degree of purity, should nevertheless be regarded as of the highest importance, and scarcely less so that the separations should be made under the most favorable conditions for the removal of the largest possible amount of impurity,—conditions which certainly cannot be claimed for the old process of fractional distillation.

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* I propose to make a series of experiments on mixtures of pure liquid substances in definite proportions, with the view to determine whether, or to what extent, the observations of Berthelot and Alluard will hold true when a mixture, of constant boiling-point, and inseparable by the old method, is distilled through my regulated condenser; and at the same time to determine also, approximately, the degree of purity attainable by my method, as a test of the capability of the process.

2. AMYL HYDRIDE = C_5H_{12}.

Specific gravity 0.6400 at 0°; 0.6275 at 14°.2; 0.6269 at 15°; 0.6249 at 17°.*

Determination of Boiling-point.— The method employed in this, and in all of the determinations of boiling-points given in this paper, unless some variation is specially mentioned, was precisely the same as that described in detail in the memoir first above referred to, page 159, and following. As constancy of boiling-point and accuracy of determination of the same are of so much importance in this investigation, and as I have deviated in some respects from the usual method of taking boiling-points, attention is specially called to what is said in that memoir on this subject; more particularly to the remarks on the question as to whether the experiment should be conducted with the bulb of the thermometer in the liquid or in the vapor. Some experiments there recorded bearing on this question are also referred to.

In order to show more fully the degree of purity of the substances, and the degree of thoroughness and accuracy of the analysis of the petroleum which this may indicate, I shall give in each case the readings of the thermometer at stated intervals during the distillation either of the whole, or very nearly the whole, of the liquid employed in the experiment, taking a fair average of these as the observed boiling-point. This, it will be observed, is a much severer test of purity, and is attended with less liability to personal error, than the more common practice of simply noting the temperature at which a certain *degree* of constancy of boiling-point is observed, omitting to indicate the limits of the distilling temperature. The custom here referred to has the additional objection, moreover, that it is liable to convey a wrong impression as to the actual degree of purity of the liquid,—not giving sufficient data to enable others to judge of this and of the accuracy of the determination, — so desirable when dealing with mixtures, like those of the hydrocarbons from petroleum, that cannot be made to yield, by the common process, liquids having a constant boiling-point, nor, properly considered, a very near approach to one, but only a pretty long "boiling-space."

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* It being too generally the custom, as I have remarked on a former occasion, to determine the specific gravities of volatile liquids at the temperature most convenient at the time of the experiment, without regard to uniformity of practice, which is so highly desirable, I have been obliged, in order to make a satisfactory comparison of other determinations with my own, to repeat the determinations at the temperatures employed by the different observers. As the results of these determinations occupy so little space, I am induced to insert them, as they were all taken with great care, and by means of a specific gravity bottle of the best construction for volatile liquids. A description of this bottle is given in Vol. IX. (N. S.) p. 144, of the Memoirs of this Academy.

In the present experiment the readings of the thermometer were as follows: —

Observed temperature of the liquid at commencement of distillation,	29°.5
" " 8 minutes later,	29°.7
" " 10 "	29°.9
" " 21 "	30°.1
" " 5 "	30°.3

At the latter temperature the liquid had distilled almost to dryness; and at 31°, six minutes later, not a drop of liquid remained in the retort. The duration of the experiment was 50 minutes, and the range of distilling temperature 1°.5, or 0°.8, if we omit the last, and doubtless least reliable, observation. As the thermometer was doubtless directly influenced by the superheated retort-bottom during the distillation of the last few drops of liquid, the last observation is considered of no value except as furnishing additional evidence of the high degree of purity of the substance, i. e. for so volatile a body of this class, obtained by fractional distillation. That it should be otherwise disregarded is shown by the fact that the bulk of the liquid passed over with so slight a variation of temperature, viz. only 0°.4, from 29°.7 to 30°.1, during the long interval of 31 minutes. The average of the first five observations, or 29°.9, is therefore taken as the observed boiling-point; which, corrected for pressure and the upper mercurial column, becomes 30°.1, being almost identical with the boiling-point that Frankland originally found for this body. The latter circumstance, with other corroborative evidence, such as the fact that my analyses gave almost invariably a somewhat larger percentage of hydrogen for the members of my 1st series than for the corresponding terms of the 2d (which may prove, however, merely accidental), has led me, while somewhat in doubt on this point, to regard this body and its homologues of the 1st series as the true hydrides of the alcohol radicals, or marsh-gas series; and the 2d series, provisionally, as the iso-hydrides of these radicals, — a term which may be appropriately retained if further examination shall furnish no stronger evidence of difference in constitution. This view is strengthened further by the fact that other observers besides Frankland and myself have found the boiling-point of hydride of amyl 30°, or thereabouts; or that it would *begin* to boil at very nearly this temperature, indicating at least the probability that it *has not a higher* boiling-point, for the gaseous butyl hydride, the next lower body of the series, would probably have been so completely expelled from the liquid during the long-continued process of fractionation that the little which might remain would not sensibly lower the boiling-point of the amyl hydride. C. G. Williams * found that amyl hydride from Boghead naphtha boiled between 30° and 40°; and a preparation of the same from similar material from cannel coal gave Schorlemmer † the boiling-point 39°–40°; but subsequently he found that a preparation from American petroleum boiled at 34°,—which comes nearer to Williams's first observation than to the lower of his own previous observations; and since he states that he obtained a larger quantity of this, which would enable him to continue longer the process of fractionation, and since a preparation from this petroleum would doubtless contain less of contaminating substances that might influence the determination, it may be inferred that his later determination is probably the more reliable of the two. But Pelouze and Cahours ‡ make the boiling-point of this body from American petroleum exactly 30°, agreeing precisely with my own determination and with that of Dr. Frankland. Furthermore, Wurtz § states that amyl hydride from amyl alcohol boils also at 30°.

The determinations above quoted having been made previously to the publication of my petroleum series, probably neither of the investigators, either of the coal or petroleum naphtha, had the remotest idea of the presence of a series isomeric with the hydrides, and therefore made no special effort to separate them; ‖ and since these determinations were evidently made on mixtures containing variable proportions, and in some cases a preponderating quantity, of these isomeric bodies, the disagreement between their results does not seem surprising, nor that the boiling-point should have been placed so high as 39°, or about that of the iso-hydride itself. In the absence of evidence, therefore, that the body described by Frankland boiling at 30° is *not* of the series of hydrides, it seems reasonable to take this, the one first described and best studied, as typical of this series; and to consider, for the present, those bodies that correspond with this in regard to their boiling-points and other properties, viz. those boiling at 0°, 60°, 90°, and 120°, respectively, as also of the same series; and those boiling at 9°, 39°, 69°, and 129°, as a series of isomers, or iso-hydrides; for it is well known with regard to the best-studied of homologous series of liquid bodies that, as a rule, a common boiling-point difference between the contiguous members prevails throughout any given series; any deviation from this being so exceptional as to justify a suspicion of error.* Nevertheless, the series of hydrides is generally represented with some of the boiling-points of one series and some of the other, while others do not agree with the true boiling-points of either series. It is hoped that the results recorded in this paper may serve to bring order out of this confusion.

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* Quarterly Journal of the Chemical Society, XV. 130.

† Journal of the Chemical Society, 1862, XV. 419.

‡ Bulletin de la Société Chimique, 1863, p. 231.

§ Comptes Rendus, 1862, LIV. 387.

‖ A re-examination by Schorlemmer has since confirmed my discovery of this series. Proceedings of the Royal Society, XIV. 468; Annalen der Chemie, CXXXV. 269.

Analysis.†

0.1935 grm. of the substance gave 0.5912 of carbonic acid, and 0.2866 of water.

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* Note Goldstein's late paper.

† The analyses given in this paper having been made, for the most part, previously to the working out of my process for combustion in oxygen gas, above referred to, it is to be understood, unless otherwise stated, that they were made, so far as relates to those boiling under 150°, by distilling the vapor of the substance into a column of ignited oxide of copper, and completing the combustion in a stream of oxygen. This method, however, was not at first successful. So long as I continued to follow the direction of Regnault to connect the bulb with the combustion tube by means of a caoutchouc tube, I was unable to avoid a loss of several per cent, occasioned, doubtless, by the escape of substance through the material of the connecting tube. That this was the probable source of error was shown by suspending a piece of this tubing in the vapor of petroleum naphtha at the common temperature, the walls of the tube soon acquiring two or three times their original thickness, from absorption of hydrocarbon vapor. During an analysis, however, no change in the appearance of the tubing was noticed, — any perceptible thickening being prevented by the heat and exposure to air carrying away the vapor as fast as absorbed. To get over this difficulty, I contrived a convenient method of making the connection with the combustion tube by means of a cork. A tube, 4 or 5 inches or more in length, with a small bulb blown in the centre, and with capillary ends, was substituted for the ordinary bulb. By leaving the tube of sufficient length on each side of the bulb, the same bulb could be repeatedly used, only requiring

			Calculated.	Found.
Carbon	Є_5	60	83.334	83.326
Hydrogen	H_{12}	12	16.666	16.448
			100.000	99.774

Determination of Vapor Density.

Temperature of balance	9°
Height of barometer	761.86 mm. at 0°
Temperature of oil bath	128°
Increment of balloon	0.2776
Capacity of balloon	235.5 c.c.
Density of vapor found	2.7642
Theory Є_5H_{12} = 4 vols.	2.4932 *

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that the capillary ends should be drawn out anew for each analysis. This bulbous tube containing the liquid to be analysed was used in the following manner. A cork fitting the combustion tube was perforated to fit one end of the bulbous tube, and the latter tightly inserted in the perforation so that the whole of the long capillary end projected beyond the cork. This end of the bulbous tube was then introduced into the combustion tube, and the cork firmly pressed into its place. The cork being a suitably flexible one, the end of the capillary tube, at the proper moment, was readily broken off against the inner surface of the combustion tube, simply by a lateral pressure against the outer half of the cork.

The distillation of the material from the bulb was better controlled by means of a heated copper bar, as described in my paper "On a Process of Organic Elementary Analysis," etc., already referred to. When no longer a trace of liquid remained in the bulbous tube, connection with the oxygen gasometer was readily made by means of a caoutchouc tube, and communication established by breaking off the capillary end within the caoutchouc connecting tube by means of pliers against the sides of the tube. Before the latter was done, however, the oxygen was turned on, in order to produce pressure from behind, and thereby prevent a possible loss from passage of vapor backward.

When making several analyses in succession, the posterior end of the combustion tube was generally found too hot at the close of an analysis to admit of being so tightly clenched with the hand as is necessary in attaching the bulbous tube; and attempts to make a good connection in this manner under such circumstances were generally unsuccessful. To overcome this difficulty, I procured an iron clamp lined with cork, the lower half of which was attached with screws to the top of the combustion furnace in such a position that the combustion tube, at a convenient point near the end, would rest on the cork in the lower half of the clamp. The upper half of the clamp being then laid on and tightly screwed down, served to hold the tube so firmly that the whole force of the hand could be applied to the cork, and thus insure a perfectly tight joint without producing the slightest disturbance of the rest of the apparatus.

* C = 0.831; H = 0.0693. [Mem.] "Repeat this determination by my process."

3. Amyl Iso-Hydride = C_5H_{12}.

Specific gravity 0.6454 at 0°; 0.6326 at 15°; 0.6306 at 17°

Determination of Boiling-point.

Observed temperature of the liquid at commencement of distillation	36°.6
Observed temperature of the liquid 38 minutes later	36°.6
" " " 20 " "	36°.7
" " " 10 " "	36°.7

Eight minutes later the liquid had all vaporized. The corrected boiling-point was found to be 37°.

Analysis.—By combustion with cupric oxide in the manner described under Hydride of Amyl, 0.1666 grm. of the substance gave 0.5068 of carbonic acid, and 0.2482 of water.

			Calculated.	Found.
Carbon	$€_5$	60	83.334	82.965
Hydrogen	H_{12}	12	16.666	16.555
			100.000	99.520

Determination of Vapor Density.

Temperature of balance	8°.5
Temperature of oil bath	129°
Height of barometer	778.8mm. at 0°
Increment of balloon	0.2255
Capacity of balloon	227.5 c.c.
Density of vapor found	2.514
Theory $€_5H_{12}$ = 4 vols.	2.4932

4. Hexyl Hydride = C_6H_{14}.

Specific gravity 0.6762 at 0°; 0.6638 at 15°.

Determination of Boiling-point.

Observed temperature of the liquid at commencement of distillation	61°.0
Observed temperature of the liquid 1 minute later	61°.2
" " " 36 minutes "	61°.2

Five mintes later it had distilled to dryness. The temperature of the boiling liquid was, therefore, absolutely constant at 61°.2

during the space of thirty-six minutes. Its corrected boiling-point is 61°27.

Analysis 1.— 0.1808 grm. of the substance gave 0.5561 of carbonic acid, and 0.2698 of water.

		Calculated		Found.
Carbon	$€_6$	72	83.72	83.884
Hydrogen	H_{14}	14	16.28	16.580
			100.00	100.464

Analysis 2.— 0.226 grm. of the substance gave 0.6968 of carbonic acid, and 0.3291 of water.

Carbon	84.089
Hydrogen	16.181
	100.270

Determination of Vapor Density.

Temperature of balance	17°
Temperature of oil bath	121°
Height of barometer	764 mm. at 10°
Increment of balloon	0.3666
Capacity of balloon	238 c.c.
Vapor density found	3.0528
Theory $€_6H_{14} = 4$ vols.	2.9735

5. HEXYL ISO-HYDRIDE = C_6H_{14}.

Specific gravity 0.689 at 0°; 0.6772 at 15°.

Determination of Boiling-point. — Conducting this experiment precisely as the preceding, the observed temperature of the liquid at the commencement of distillation was 68°.1, and it remained absolutely constant during the long space of 52 minutes, distilling down to a very small residue, which was left in the retort at this temperature. The corrected boiling-point was found to be 68°.5.

Analysis 1.— 0.1363 grm. of the substance gave 0.4214 of carbonic acid, and 0.194 of water.

		Calculated.		Found.
Carbon	$€_6$	72	83.72	84.43
Hydrogen	H_{14}	14	16.28	15.81
			100.00	100.24

Analysis 2.— 0.1700 grm. of the substance gave 0.5256 of carbonic acid, and 0.2412 of water.

		Calculated.		Found.
Carbon	Ꞓ_6	72	83.72	84.321
Hydrogen	H_{14}	14	16.28	15.765
			100.00	100.086

Determination of Vapor Density.

Temperature of balance	16°
Temperature of oil bath	129°
Height of barometer	762 mm. at 8°
Increment of balloon	0.8829
Capacity of balloon	262 c.c.
Density of vapor found	3.038
Theory Ꞓ_6H_{14} = 4 vols.	2.9737

6. HEPTYL HYDRIDE = C_7H_{16}.

Specific gravity 0.7183 at 0° ; 0.7065 at 15°.
Specific gravity after treatment with nitric acid 0.7033.

Determination of Boiling-point.

Observed	temperature	at commencement of distillation	88°.7
"	"	10 minutes later	88°.9
"	"	17 " "	89°
"	"	13 " "	89°.1
"	"	5 " "	89°.3
"	"	10 " "	89°.7

having distilled quite to dryness. Applying the usual corrections to the number 89°, the corrected boiling-point is found to be 90°.4. After treatment of a portion of this body with nitric acid, its corrected boiling-point was 90°.53. This experiment was made, however, on a very small quantity of liquid, and would hardly justify the conclusion that the acid had really effected a change of the boiling-point.

Analysis 1.— 0.2268 grm. of the substance gave 0.7031 of carbonic acid, and 0.3165 of water.

		Calculated.		Found.
Carbon	Ꞓ_7	84	84.00	84.55
Hydrogen	H_{16}	16	16.00	15.51
			100.00	100.06

Analysis 2. — 0.2187 grm. of the substance gave 0.6766 of carbonic acid, and 0.3064 of water.

		Calculated.		Found.
Carbon	Ȼ_7	84	84.00	84.38
Hydrogen	H_{16}	16	16.00	15.57
			100.00	99.95

Determination of Vapor Density.

Temperature of balance	12°.5
Temperature of oil bath	134°
Height of barometer	746 mm. at 6°
Increment of balloon	0.4383
Capacity of balloon	242 c.c.
Density of vapor found	3.547
Theory $\text{Ȼ}_7H_{16} = 4$ vols.	3.458

7. HEPTYL ISO-HYDRIDE = C_7H_{16}.

Specific gravity 0.7299 at 0°; 0.7184 at 15°. After treatment with an excess of monohydrated nitric acid, specific gravity 0.7048 at 16°.

Determination of Boiling-point.

Observed temperature of the liquid at commencement of distillation	96°.6
Observed temperature of the liquid 10 minutes later	96°.8
" " " 15 " "	96°.9
" " " 20 " "	97°.2

Having had occasion to leave the experiment for a few moments at this juncture, on returning ten minutes later it was found that the liquid had distilled to dryness. The average of the observations 96°.8 and 97°.2 is 97°. Applying the proper corrections, we find the corrected boiling-point to be 98°.1.

After treatment of a small portion of this oil with monohydrated nitric acid, its corrected boiling-point was then 97°.85; but, as in the last experiment, the quantity of oil operated upon was too small to admit of making a very exact determination.

Analysis. — 0.2073 grm. of the substance gave 0.6469 of carbonic acid, and 0.2862 of water.

		Calculated.		Found.
Carbon	Ꞓ_7	84	84.00	85.11
Hydrogen	H_{16}	16	16.00	15.34
			100.00	100.45

Determination of Vapor Density.

Temperature of balance	17°
Temperature of oil bath	138°.5
Height of barometer	763.4 mm. at 9°
Increment of balloon	0.4236
Capacity of balloon	228.5 c.c.
Density of vapor found	3.546
Theory Ꞓ_7H_{16} = 4 vols.	3.389

8. OCTYL HYDRIDE = C_8H_{18}.

Specific gravity 0.7374 at 0°; 0.7262 at 15°.

Determination of Boiling-point.— The quantity of liquid at my disposal for this experiment was considerably smaller than that employed in the determinations above detailed; therefore, instead of using a retort, the distillation was made from a large, long-necked bulb. Since in this case the whole of the mercury was situated below the cork, and surrounded by the hot ascending vapors, no correction for the mercurial column is required.

Observed temperature of the liquid at commencement of distillation	119°.1
Observed temperature of the liquid 5 minutes later	119°.2
" " " 10 " "	119°.4
" " " 2 " "	119°.6
" " " 3 " "	120°

At the latter point it had distilled nearly to dryness. This determination was made under normal atmospheric pressure, and therefore requires no correction. Taking the average of the five observations, we find the boiling-point to be 119°.5.

Analysis.[*]

Determination of Vapor Density.

Temperature of balance	12°
Temperature of oil bath	198°
Height of barometer	777 mm. at 9°
Increment of balloon	0.3889
Capacity of balloon	215.5 c.c.
Density of vapor found	3.992
Theory $Ȼ_8H_{18}$ = 4 vols.	3.9425

9. OCTYL ISO-HYDRIDE = C_8H_{18}.

Specific gravity 0.7516 at 0°; 0.7430 at 15°.

Determination of Boiling-point. — This experiment was conducted in the manner described under octyl hydride, and for the same reason there stated. Atmospheric pressure normal.

Observed temperature of the liquid at commencement of distillation	126°.8
Observed temperature of the liquid 10 minutes later	127°.0
" " " 5 " "	127°.2
" " " 4 " "	127°.4
" " " 6 " "	129°.1

Average boiling-point 127°.6.

Analysis.[†]

Determination of Vapor Density.

Temperature of balance	13°
Temperature of oil bath	211°
Height of barometer	777 mm. at 9°
Increment of balloon	0.3662
Capacity of balloon	212 c.c.
Density of vapor found	3.9900
Theory $Ȼ_8H_{18}$ = 4 vols.	3.9425

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[*] A memorandum written by the author in pencil on the margin of his MS. reads, after the word Analysis, "Not made, August, 1868."

[†] A note by the author reads: "Analysis not yet made, August, 1868." Another memorandum reads: "Storer and W. [in their memoir on the Exam-

10. NONYL HYDRIDE = C_9H_{20}.

Specific gravity 0.7555 at 0°; 0.7447 at 15°.

Determination of Boiling-point.

Observed temperature of the liquid at commencement of distillation						148°.7
Observed temperature	of the	liquid	15	minutes	later	148°.7
"	"	"	15	"	"	148°.9
"	"	"	5	"	"	149°.1
"	"	"	13	"	"	149°.4
"	"	"	2	"	"	149°.7

Average of observations 149°.2. Corrected boiling-point 150°.6. Average of two determinations 150°.8.

Analysis.— 0.1841 grm. of the substance gave 0.5765 of carbonic acid, and 0.2526 of water.

		Calculated.		Found.
Carbon	Ꞓ_9	108	84.375	85.40
Hydrogen	H_{20}	20	15.625	15.24
			100.000	100.64

Determination of Vapor Density.

Temperature of balance	18°.5
Temperature of oil bath	220°
Height of barometer	756.3 mm. at 17°
Increment of balloon	0.4649
Capacity of balloon	234 c.c.
Density of vapor found	4.460
Theory Ꞓ_9H_{20} = 4 vols.	4.426

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ination of a Hydrocarbon Naphtha, obtained from the products of the Destructive Distillation of Lime-soap, Memoirs of the American Academy, 1865 (N. S.), IX. 177] say H[ydride] of C[apryl] boils at 128°, near bottom of page 195, and elsewhere? [i. e. page 194]. Perhaps I should call the '8 bodies' [viz. those boiling at 8°, 38°, and so on] hydrides, and the '10 bodies' [boiling at 0°, 30°, etc.] iso-hydrides? See Schorlemmer's late work, and compare with Wurtz's bodies from amyl alcohol." It appears, however, that this hesitancy was but momentary, for, as is to be seen above, on pages 70, 71, he finally accepted Frankland's hydride of amyl, boiling at 30°, as the prototype of the normal hydrides, and relegated the substance boiling at 128° to the second series, of which it is the last term. Note by F. H. Storer.

$\text{Ꞓ}_n\text{H}_{2n}$ Series.

1 Rutylene = $C_{10}H_{20}$.

Specific gravity 0.7703 at 0°; 0.7598 at 15°.

1. *Determination of Boiling-point.*— By the thermometer employed, water was found to boil at 101°.1.

Observed temperature of liquid at commencement of distillation	172°.5
Observed temperature of liquid 7 minutes later	172°.7
" " " 8 " "	173°
" " " 5 " "	173°.3
" " " 5 " "	173°.7
" " " 2 " "	174°

Had distilled nearly to dryness. Taking the average of the six observations, and applying the proper corrections for pressure and the upper mercurial column, and also deducting 1°.1 for the error of the thermometer, the corrected boiling-point is found to be 174°.9.

2. *Determination of Boiling-point.* — By the thermometer employed water boiled at 100°.5. This experiment was conducted precisely as the last, and the material employed was the same.

Observed temperature of liquid at beginning of distillation	172°.3
Observed temperature of liquid 5 minutes later	172°.5
" " " 13 " "	172°.8
" " " 22 " "	173°
" " " 10 " "	172°.9
" " " 10 " "	172°.9
" " " 5 " "	173°

Five minutes later had distilled nearly to dryness, the temperature having risen to 173°.8. Taking 173° as the observed boiling-point, and making the proper corrections for pressure and the mercurial column, and also deducting the error of the thermometer, 0°.5, gives 175°.3 as the corrected boiling-point.

Analysis 1. — 0.1257 grm. of the substance gave 0.3951 of carbonic acid, and 0.1713 of water.

		Calculated.		Found.
Carbon	$Ȼ_{10}$	120	85.71	85.720
Hydrogen	H_{20}	20	14.29	15.139
			100.00	100.859

Analysis 2. — 0.2689 grm. of the substance gave 0.8398 of carbonic acid, and 0.3577 of water.

		Calculated.		Found.
Carbon	$Ȼ_{10}$	120	85.71	85.18
Hydrogen	H_{20}	20	14.29	14.78
			100.00	99.96

Determination of Vapor Density.

Temperature of balance	18°
Temperature of oil bath	236°
Height of barometer	757.4 mm. at 17°
Increment of balloon	0.5743
Capacity of balloon	249 c.c.
Density of vapor found	5.066
Theory $Ȼ_{10}H_{20}$ = 4 vols.	4.843

2. MARGARYLENE = $C_{11}H_{22}$.

Specific gravity, 0.7822 at 0° ; 0.7721 at 15°.

Determination of Boiling-point.

Observed temperature of liquid at commencement of distillation	192°.5
Observed temperature of liquid 3 minutes later	192°.7
" " " 5 " "	193°.
" " " 10 " "	193°.5

Five minutes later the bottom of the retort had become nearly dry, the temperature having reached 194°.5. The average of the first four observations is 193° ; and the corrected boiling-point 195°.4. A second determination, by another thermometer, gave the corrected boiling-point 196°.2; the average of the two determinations being 195°.8.

Analysis 1. — 0.197 grm. of the substance gave 0.6183 of carbonic acid, and 0.2624 of water.

		Calculated.		Found.
Carbon	$Ȼ_{11}$	132	85.71	85.60
Hydrogen	H_{22}	22	14.29	14.80
			100.00	100.40

Analysis 2. — 0.1997 grm. of the substance gave 0.6248 of carbonic acid, and 0.2633 of water.

		Calculated.		Found.
Carbon	$Ȼ_{11}$	132	85.71	85.33
Hydrogen	H_{22}	22	14.29	14.65
			100.00	99.98

Determination of Vapor Density.

Temperature of balance	14°.5
Temperature of oil bath	250°
Height of barometer	767 mm. at 13°
Increment of balloon	0.6227
Capacity of balloon	247.5 c.c.
Density of vapor found	5.480
Theory $Ȼ_{11}H_{22}$ = 4 vols.	5.327

3. LAURYLENE = $C_{12}H_{24}$.

Specific gravity 0.7905 at 0°; 0.7804 at 15°.

1. *Determination of Boiling-point.* — By the thermometer employed, water boiled at 100°.5.

Observed temperature of the liquid at commencement of distillation	212°
Observed temperature of the liquid 16 minutes later	212°.3
" " " 9 " "	212°.7
" " " 4 " "	213°

Three minutes later the boiling-temperature was 214°, having distilled nearly to dryness. The average of the first five observations is 212°.5. Deducting the error of the thermometer, 0°.5, and making the usual corrections for pressure and the upper column of mercury, the corrected boiling-point is found to be 216°.8.

2. *Determination of Boiling-point.* — The conditions of this experiment were the same as the last, with the exception that by the thermometer employed, water boiled at 101°.1.

Observed temperature of the liquid at beginning of distillation	210°.3
Observed temperature of the liquid 5 minutes later	210°.7
" " " 3 " "	211°
" " " 5 " "	211°.5
" " " 4 " "	212°

Had distilled nearly to dryness at 212°5. Average of the six observations, 211°; corrected boiling-point, 215°.5. Average of both determinations, 216°.2.

Analysis 1. — 0.1401 grm. of the substance gave 0.4349 of carbonic acid, and 0.1872 of water.

		Calculated.		Found
Carbon	€_{12}	144	85.71	84.66
Hydrogen	H_{24}	24	14.29	14.85
			100.00	99.51

Analysis 2. — 0.1934 grm. of the substance gave 0.608 of carbonic acid, and 0.2551 of water.

		Calculated.		Found.
Carbon	€_{12}	144	85.71	85.74
Hydrogen	H_{24}	24	14.29	14.66
			100.00	100.40

Determination of Vapor Density.

Temperature of balance	12°.5
Temperature of oil bath	274°
Height of barometer	762.6 mm. at 4°
Increment of balloon	0.6905
Capacity of balloon	253 c.c.

Density of vapor found	6.090
Theory, $\text{€}_{12}H_{24}$ = 4 vols.	5.812

Having already given tables of the boiling-points, — the determinations of which are above detailed, — with such deductions and remarks as seemed appropriate, I will now proceed to treat the other results in a similar manner. A comparison of these results, which the tables will greatly facilitate, will bring to view some interesting relations.

TABLE I. — *Showing the Difference of Specific Gravity corresponding to Difference of Boiling-point of the Bodies obtained from Pennsylvania Petroleum, arranged in the Order of the Boiling-points, regardless of Serial Classification or Elementary Difference; and also showing the Differences of Specific Gravity at* 0° *and* 15°.

Name.	Formula.	Boiling-point.	Specific Gravity at 0°.	Difference of Boiling-point.	Difference of Specific Gravity.	Specific Gravity at 15°.	Difference of Sp. Gr. at 0° and 15°
Butyl Hydride	C_4H_{10}	0°.0*	0.6000*	° —	—	—	—
" Isohydride	"	8–9	0.6107	8.5	0.0107	0.5967†	0.0104†
Amyl Hydride	C_5H_{12}	30.2	0.6400	21.3	0.0293	0.6269	0.0131
" Isohydride	"	37.0	0.6454	6.8	0.0054	0.6326	0.0128
Hexyl Hydride	C_6H_{14}	61.3	0.6762	24.3	0.0308	0.6638	0.0124
" Isohydride	"	68.5	0.6893	7.2	0.0131	0.6772	0.0121
Heptyl Hydride	C_7H_{16}	90.4	0.7183	21.9	0.0290	0.7065	0.0118
" Isohydride	"	98.1	0.7299	7.7	0.0116	0.7184	0.0115
Octyl Hydride	C_8H_{18}	119.5	0.7374	21.4	0.0075	0.7262	0.0112
" Isohydride	"	127.6	0.7516	8.1	0.0142	0.7430	0.0086
Nonyl Hydride	C_9H_{20}	150.8	0.7555	23.2	0.0039	0.7447	0.0108
Rutylene	$C_{10}H_{20}$	174.9	0.7703	24.1	0.0148	0.7598	0.0105
Margarylene	$C_{11}H_{22}$	195.8	0.7822	20.9	0.0119	0.7721	0.0101
Laurylene	$C_{12}H_{24}$	216.2	0.7905	20.4	0.0083	0.7804	0.0101

Average difference of boiling-point between the corresponding hydrides and isohydrides 7°.7 nearly.

* Ronald's determination. † Calculated.

TABLE II. — *Showing the Difference of Specific Gravity at* 0° *corresponding to the Common Difference of about* 30° *between their Boiling-points, and to the Elementary Difference of* CH_2 *in the Series of Hydrides.*

Name.	Formula.	Boiling-point.	Specific Gravity.	Elementary Difference.	Difference of Boiling-point.	Difference of Specific Gravity.
Butyl Hydride	C_4H_{10}	0.0*	0.6000*	—	—	—
Amyl "	C_5H_{12}	30.2	0.6400	CH_2	30.2	0.0400
Hexyl "	C_6H_{14}	61.3	0.6762	CH_2	31.1	0.0362
Heptyl "	C_7H_{16}	90.4	0.7183	CH_2	29.1	0.0421
Octyl "	C_8H_{18}	119.5	0.7374	CH_2	29.1	0.0191
Nonyl "	C_9H_{20}	150.8	0.7555	CH_2	31.3	0.0181

Average difference of boiling-point 30°.16.
" " specific gravity 0.0311.
" " " " below 100° of boiling-point, 0.0394; and above 100°, 0.0186.

TABLE III. — *Showing the Difference of Specific Gravity at* 0° *corresponding to the Common Difference of about* 30° *between their Boiling-points, and to the Elementary Difference of* CH_2 *in the Series of Isohydrides.*

Name.	Formula.	Boiling-point.	Specific Gravity.	Elementary Difference.	Difference of Boiling-point.	Difference of Specific Gravity.
Butyl Isohydride	C_4H_{10}	8–9	0.6107	—	—	—
Amyl "	C_5H_{12}	37.0	0.6454	CH_2	29.5	0.0347
Hexyl "	C_6H_{14}	68.5	0.6893	CH_2	31.5	0.0439
Heptyl "	C_7H_{16}	98.1	0.7299	CH_2	29.6	0.0406
Octyl "	C_8H_{18}	127.6	0.7516	CH_2	29.5	0.0217

Average difference of boiling-point, 30°.03.
" " specific gravity, 0.0352.
" " " " below 100° of boiling-point, 0.0397.
Difference of specific gravity above 180° of boiling-point, 0.0217.

*** Ronald's determination.**

TABLE IV. — *Showing the Difference of Specific Gravity at 0° corresponding to the Common Difference of about 20° between the Boiling-points, and to the Elementary Difference of CH_2 in the C_nH_{2n} Series.*

Name.	Formula.	Boiling-point.	Specific Gravity.	Elementary Difference.	Difference of Boiling-point.	Difference of Specific Gravity.
Rutylene	$C_{10}H_{20}$	174.9	0.7703	—	—	—
Margarylene	$C_{11}H_{22}$	195.8	0.7822	CH_2	20.9	0.0119
Laurylene	$C_{12}H_{24}$	216.2	0.7905	CH_2	20.4	0.0083

NOTE ON A MEMOIR BY C. SCHORLEMMER.

There was found among Warren's papers, in the same portfolio with the manuscript of the foregoing memoir, a printed copy of a memoir "On the Normal Paraffins" (taken from the Philosophical Transactions, 1872, Vol. CLXXII.), which had been presented to Warren by its author, Dr. Schorlemmer. Upon the last page of this presentation copy Warren had written in pencil some memoranda which, under the peculiar circumstances of the case, seem to be worthy of being put upon record.

For the sake of clearness, page 123 of Schorlemmer's memoir is here copied, in quotation marks, together with the memoranda which stand written upon that page of the memoir in Warren's handwriting.

It is to be observed that both the side-note, at the left of the tabular matter, as printed on the next page, and the column of figures headed "Difference found," at the right of the table, were written by Warren. The asterisk also, affixed to the word "Butane" in the table, and the foot-note to which this asterisk refers, are copied from Warren's memoranda.

Homologues of Marsh Gas.

			"Boiling-points. Mean found.	Calculated.	Difference."	Difference found.	
	"CH_4	Methane					
	C_2H_6	Ethane					
	C_3H_8	Propane					
	C_4H_{10}	Butane*	1°	1°			
37° to 39°, p. 114	C_5H_{12}	Pentane	38	38	37	37	
600 c.c. 97°.5 to 98°. Remainder 98° to 99°, p 121	C_6H_{14}	Hexane	70	71	33 = 37–4	32	37 − 2 = 5
	C_7H_{16}	Heptane	99	100	29 = 33–4	29	
	C_8H_{18}	Octane	124	125	25 = 29–4	25	
	$C_{12}H_{26}$	Dodecane	202	201	4 × 19		
	$C_{16}H_{34}$	Hecdecane	278	278	4 × 19"		

"In calculating the boiling-points, it was assumed, as appears to be the case, that the difference decreases regularly by 4 until it reaches the well known difference 19°."

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* This Butane, C_4H_{10}, corresponds to the first member of my first series, which I call the normal hydrides of the alcohol radicals, the series above given being isomeric with the hydrides.

According to my observations "Butane" should boil at about 8° to 9°, and its isomeride at 0° instead of 1°. Taking 8° to 9° as the boiling-point of Butane, the difference of boiling-point between it and "Pentane" would be 29° to 30°.

Taking 29° to 30° as the starting point for his calculated differences, and deducting 4° successively, we have

29° to 30° − 4° = 25° to 26°	Pentane and Hexane.
25° to 26° − 4° = 21° to 22°	Hexane and Heptane.
21° to 22° − 4° = 17° to 18°	Heptane and Octane.